Novel Filtration Membranes Fabricated by Polyaniline Nanofibers

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Abstract

A key advance in the field of nanotechnology is the development of self-assembling polyaniline carbon nanofibers. Hydrophilic polyaniline nanostructures offer great promise for the field of filtration technology. The properties of these hydrophilic membranes could significantly reduce fouling of membranes by adsorption of natural organic matter (NOM) foulants. Three different types of the membranes were fabricated based on polyaniline (PANI) nanostructures. The first one is the composite type of membrane consisting of a support with a large pore size, dispersed carbon nanofibers (CNFs), and a final polyaniline nanostructured coating. The second form is the thermal crosslinked free-standing porous films of polyaniline nanofibers, and the final form is the *in-situ* deposited polyaniline nanostructures grown on the commercially available microfiltration membranes such as cellulose acetate and polyethersulfone membranes. All three membrane types were created and the results from the optimization and comparison of these three types of membranes are discussed. The best membrane candidates in their class were evaluated qualitatively for mechanical durability and uniformity and/or physically for water filtration performance properties such as pure water flux and fouling potential.

The most successful membranes were compared with commercially available polysulfone, cellulose acetate and cellulose ester membranes. It was found that the thin film membranes had problems with physical integrity and the composite membranes had the most issues with consistency between batches. Thus, the majority of experimental variables such as the impact of the PANI dopants, doped state, and pH of the foulant solution were investigated using the PANI nanofiber coated membranes. It was found that PANI coatings did not improve the fouling performance over the reference under any of these conditions and that the PANI nanofiber coating increased the hydrophobicity of commercially available membranes.

Introduction

Water scarcity and the health issues arising from poorly treated water necessitate the development of improved methods of water purification. Approximately one third of the global population lives in countries with moderate to high water stress with the impact of water scarcity disproportionately impacting the poor (1). One promising field to meet these pressing needs is membrane technologies, but widespread use is limited due to complications with membrane fouling (2, 3). Fouling by particles and natural organic matter (NOM) significantly reduces the permeate flux and the lifespan of the membranes. Hydrophilic membranes have been shown to reduce fouling due to NOM species (3). The emerging field of nanotechnology offers great promise to specifically tailor membranes to exhibit ideal properties for purification such as hydrophilicity. New super-hydrophilic membranes, with a water contact angle of less than 5°, membranes have been created with polyaniline coated-carbon nanofibers (4). The super hydrophilic nature of these membranes is attributed to the surface roughness effect of the carbon nanofibers (5). This phenomenon is illustrated in Figure 1 below.

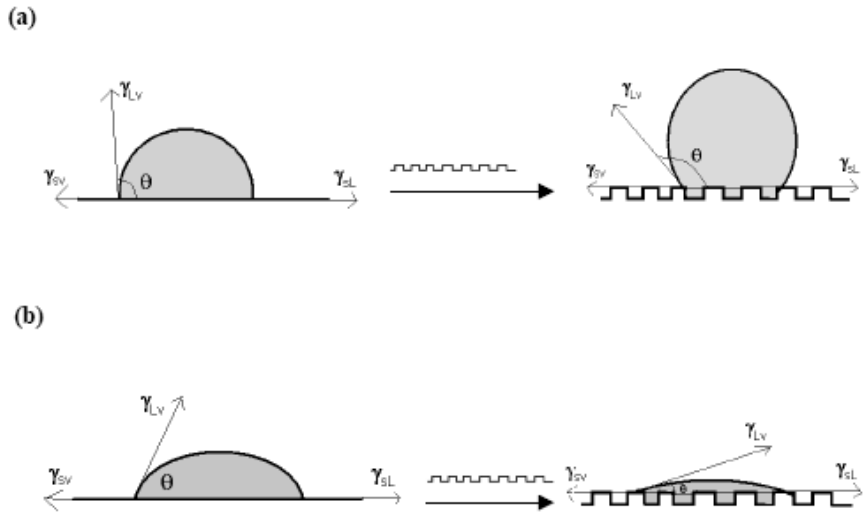

Figure 1: Surface Roughness Effect on a) Hydrophobicity and b) Hydrophilicity[5]

Polyaniline can self-assemble to form elongated 1-D nanostructures under certain synthesis conditions (6). Promising applications of the polyaniline nanofibers explored have included nano/microelectronics, metallic corrosion protection, sensors, and actuators (7). Using self-assembly techniques, membranes are created with polyaniline (PANI), creating a super-hydrophilic surface (4).

This work focuses on three main forms of PANI nanofiber membranes: a thermally-cured thin film, a composite membrane, a PANI nanofiber-coated membrane. For the composite membranes, a thin active layer, about twenty nanometers thick, is formed on top carbon nanofibers supported by another substrate. The hydrophilic properties of these membranes offer great promise in the field of water purification to significantly reduce fouling, and thus reduce the cost of operation (3, 7).

Background

Previous research has found that nanofibrous composite membranes exhibit much higher flux than conventional porous membranes with similar pore sizes for water filtration. One reason for such improvements is the high porosity observed- about 70%. A composite membrane with a non-woven microfibrous support, a mid-layer consisting of an electrospun nanofibrous support and a final hydrophilic coating of chitosan, exhibited a flux rate that was an order of magnitude higher than commercial nanofiltration membranes (9).

Data from similar polysulfone (PS) ultrafiltration membranes blended with polyaniline showed a pure water flux of 2 to 2.5 times greater than the original PS membrane and greater anti-fouling properties (7). The new polyaniline nanofiber membranes investigated in this research also offer great promise to use nanotechnology and self-assembly techniques to design and fabricate new purification methods to meet and exceed performance criteria of existing membranes. These novel membranes can be modified to be super hydrophilic as demonstrated below in Figure 2.

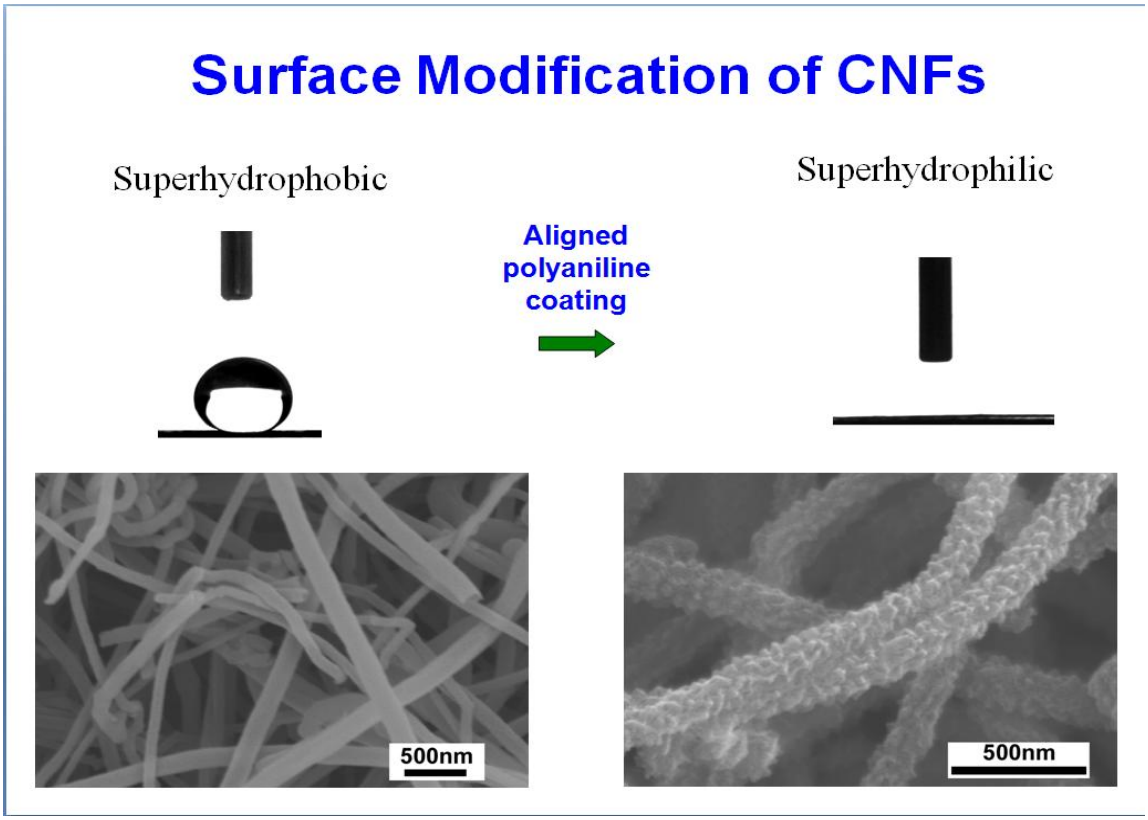

Figure 2: Surface Modification of CNFs

Fouling is of great concern for membranes because it significantly reduces the flux over time. Dissolved natural organic matter (NOM) is one major cause of fouling (3).There are several different ways to experimentally measure the impact of fouling on a membrane due to NOM. The first is using a natural surface water source filtered to remove all dissolved solids. The second approach is to use a reference NOM substance such as humic acid. Humic substances constitute a major fraction of dissolved NOM, and thus make excellent reference substances for modeling fouling.

Humic acids have molecular weights of 1000-5000 and contain both aromatic and aliphatic components, and the functional groups are mainly carboxylic and phenolic (3). An example structure of the humic acid molecule is shown below in Figure 3.

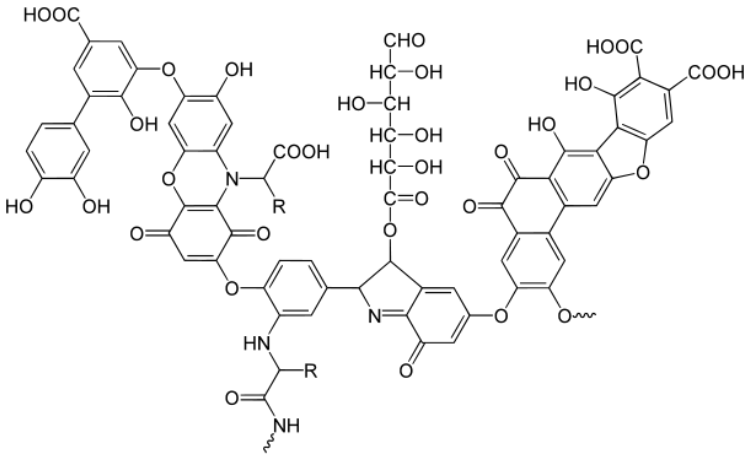

Figure 3: Proposed Structure of Humic Acid[8]

Due to the amphiphilic nature, the humic acid molecule behaves differently under different pH conditions. It is proposed that the dissolved humic acid structure is a random coil with an electric charge. The electric charge, mainly a result of the ionization of the carboxyl groups, causes the repulsion and the expansion of the coil at different pH values. As a result, studies have shown a decrease in adsorption of humic acid to regenerated cellulose membranes at higher pH values (10). Since the membranes evaluated in this study are also hydrophilic, this behavior is expected to be observed.

Objective

Work was conducted to synthesize membranes that exhibit improved properties for water treatment, as measured by pure water flux and fouling potential. The parameters investigated for the thermally-cured thin film membranes include the curing time & temperature, the acid type and the quantity of polyaniline fibers deposited. The parameters investigated for the composite membranes include the substrate, the binding agent, the dispersant and dispersion method for the CNFs. The parameters investigated in the polyaniline nanofiber coating for both the composite and the commercially coated membranes include the dopants and the doped state. Once the membranes were synthesized, they were evaluated qualitatively for mechanical durability and uniformity and/or for water filtration properties such as pure water flux, and fouling potential. The quantitative results were then compared with existing commercial membranes.

Description of Polyaniline Nanofiber Membranes

Three main forms of polyaniline nanofiber membranes were synthesized for the application of water purification. The first type is a composite membrane with a thin active layer (<10nm) of the polyaniline nanofibers. The second type of membrane is the thermal cross-linked free standing film, and the final form is a coated commercially available membrane. A detailed discussion of these three types of membranes is presented below.

Polyaniline Nanofiber Thermal Cross-linked Films

The first type of polyaniline nanofiber membrane was the thermally-cured thin film. This was created by depositing a solution of purified polyaniline nanofibers onto a silicon substrate, and then thermally curing them at 260°C using a hotplate. An image of this type of membrane can be seen in Figure 4. Work was conducted to optimize the membrane uniformity, but the membrane was too mechanically weak to function under the transmembrane pressures necessary to generate flux.

Figure 4: Image of Polyanline Thermal Cross-linked Membrane.

At the end of many synthesis experiments, it was determined that the free-standing film simply presented too many challenges for the scope of this honors thesis research. Thus, the focus was shifted to the coating of available commercial membranes.

Composite Membranes

The idea behind the composite membrane is to create a three layer membrane consisting of a highly porous support layer and then a layer of carbon nanofibers that is then coated with a thin layer of polyanline fibers. The major challenge with this type of membrane is its physical durability. The major problems encountered with these membranes were an inconsistent pore size due to an uneven distribution of CNFs, detachment of the CNFs from the membranes during operation and tearing of the membrane during operation. A lengthy discussion of these challenges and the proposed solution is discussed in the Results section. An image of composite membrane can be seen in Figure 5.

Figure 5: Image of CNF Composite Membrane

Polyaniline Nanofiber-Coated Commercial Membranes

The final form of polyaniline nanofiber membranes is the polyaniline nanofiber-coated commercial membranes. Membranes can be coated with polyaniline nanofibers, and these membranes are particularly useful for determining the impact of various polyanline synthesis conditions and their impact on membrane performance. While the thermally-cured and composite membranes are difficult to synthesize and present challenges with consistency between batches, the advantage of polyaniline nanofiber coated membranes is their relative consistency. Commercially available membranes have uniform pore size and material

consistency. The parameters investigated, different dopants and doped states, impact the coating thickness and membrane performance. The variation in polyaniline coating manifests itself in different colors illustrated in Figure 6.

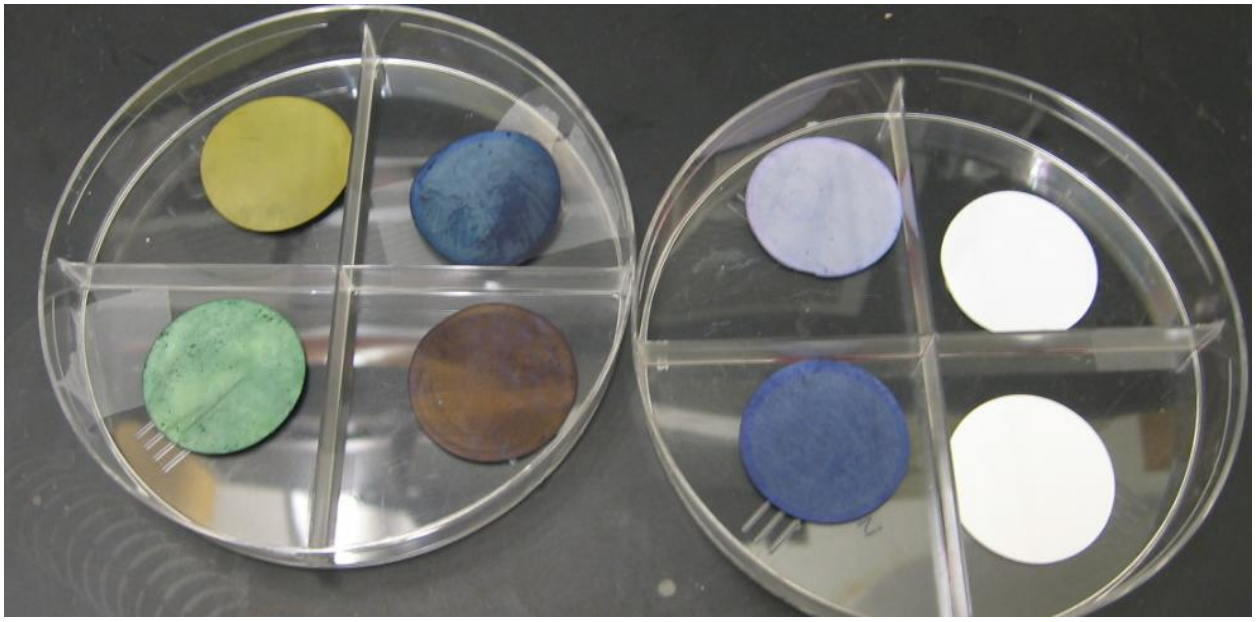

Figure 6: Various PANI Nanofiber-Coated Membrane

Two of the types of membranes coated are Polyethersulfone (PES) and Cellulose Acetate and Cellulose Ester. Images of these two membranes are in Figure 7 and 8. These membranes are all relatively hydrophilic and commonly used in current water filtration processes. Published data suggests that contact angles for cellulose acetate range from 46° to 53.3°, and for PES range from 44.7° to 69.7° (11).

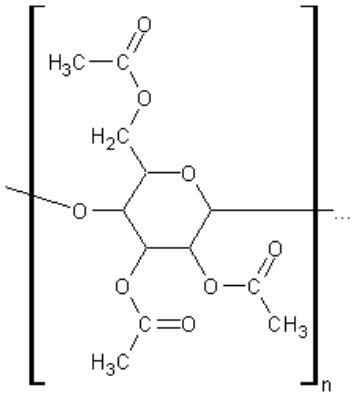

Figure 7: Cellulose Acetate Structure

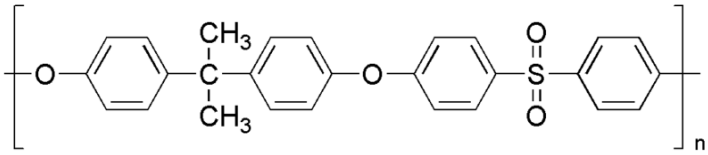

Figure 8: PES Structure

Materials

The Aniline (ACS reagent, ≥99.5%), Ammonium persulfate, Sodium Bicarbonate, Hydrochloric acid, Poly(4-styrenesulfonic acid) solution, and 4-Dodecylbenzenesulfonic acid were purchased from Sigma-Aldrich. The 0.45µm and 1.2µm Mixed Cellulose Ester 25mm diameter membranes were purchased from Millipore Corporation. The 0.45µm Cellulose Acetate and the 0.45µm Polyethersulfone 25mm diameter membranes were purchased from GE Osmotics. The carbon nanofibers (CNFs) were purchased from Applied Science Inc. The Suwannee River Humic Acid Standard was purchased from the International Humic Substances Society (IHSS).

Experimental Methods

Polyaniline Nanofiber Synthesis

Aniline is dissolved in a small portion of the 1M dopant acid and carefully added to a solution of ammonium peroxydisulfate (APS) dissolved in the remainder of the dopants acid.[5] This reaction can be referenced below in Figure 9.

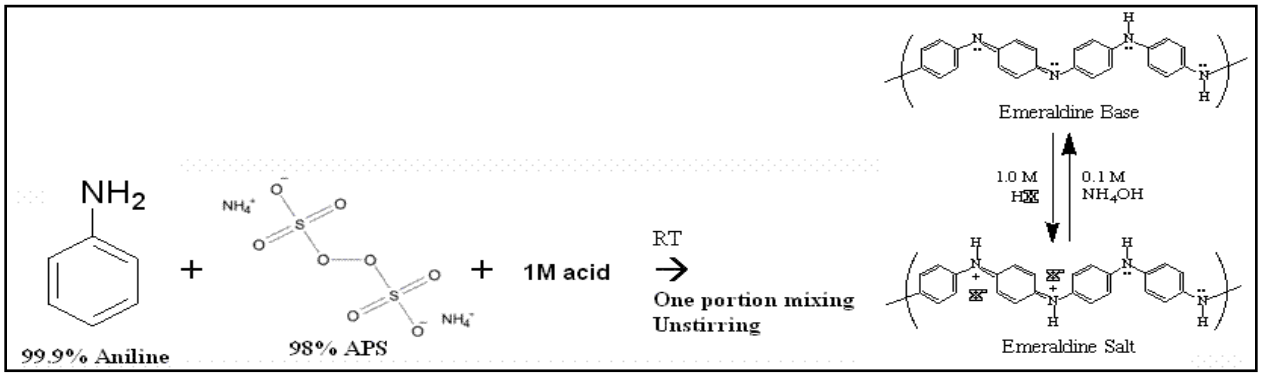

Figure 9: Summary of Polyaniline Reaction[12]

A sample formula used in the polyaniline nanofiber synthesis is this research is presented below in Figure 10.

	Aniline	**APS**
MW	93.18	228.20
Molar Ratio	1.5	1
Grams	0.187	0.310
mMoles	2.0	1.46
[M]	0.1M	0.067M
Vol. of Acid	18 mL	2 mL
Total Volume Acid	20 mL	

Figure 10: Polyaniline Nanofiber Recipe

After the addition of the aniline, the solution is briefly agitated to ensure proper mixing. The reaction is then carried out without disturbance at room temperature for the desired time interval, typically four to twenty four hours. Images of the progression of this reaction are available in Figure 11. After the nanofibers are formed, they are purified by dialysis. The solution of nanofibers are removed from the beaker and placed into dialysis tubing with a molecular weight cut-off between 12,000-14,000. The tubes are clamped shut and placed in a large beaker of deionized water which should be replaced every two to four hours. The reaction is carried out for twenty four hours or until the water surrounding the dialysis tubing is no longer acidic.

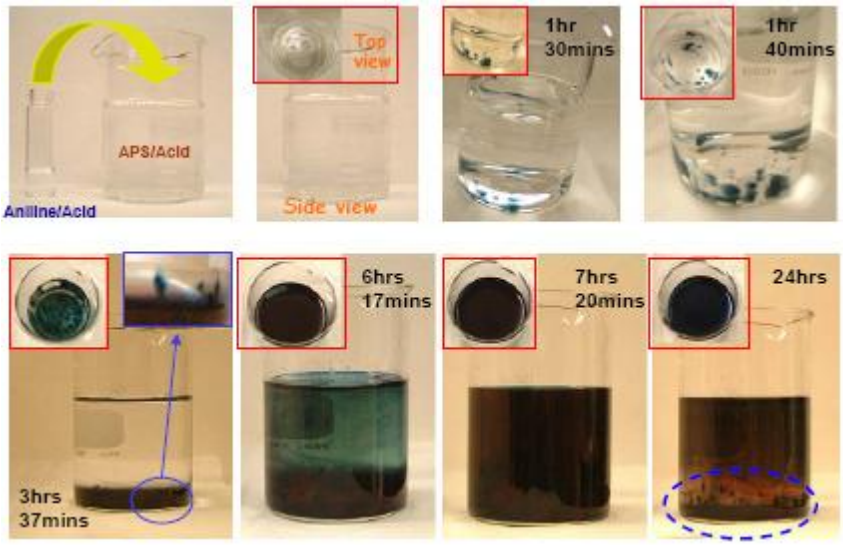

Figure 11: Images Illustrating Dilute Polymerization[5]

In Figure 9, both the doped and dedoped states are shown. If the dedoped state is desired, the fibers are then treated with 0.1M ammonium hydroxide for 48 hours and then thoroughly washed with deionized water. This step removes the acid dopants from the membrane structure to form the emeraldine base.

This procedure can also be modified to coat membranes. The membranes are placed into the Aniline/APS solution after mixing. The membranes are then removed and washed with deionized water.

Composite Membranes

To create a dispersion of 0.50wt% CNF in deionized water, 0.5 wt% sodium dodecyl sulfate (SDS), the dispersant, was first dissolved in the water. Then, the CNFs are added and dispersed using a horn sonicator at 85% amplitude for thirty minutes. Ten grams of the CNF dispersion is then deposited on the support substrate, Whatman #4 filter paper using a Buchner funnel to pull a vacuum. The permeate is then collected and run through the setup a total of three times. Next, the coated substrate must be fully dried using a vacuum oven at room temperature for one hour. If desired, a binding agent can be added at this time to the dried membrane. The 70mm diameter of the substrate coated with CNF must be cut to form four smaller membranes with a diameter of 25mm if used for the Amicon dead-end filtration set-up. Finally, the membranes can be coated with polyaniline nanofibers in the process outlined above. This process is seen in Figure 12.

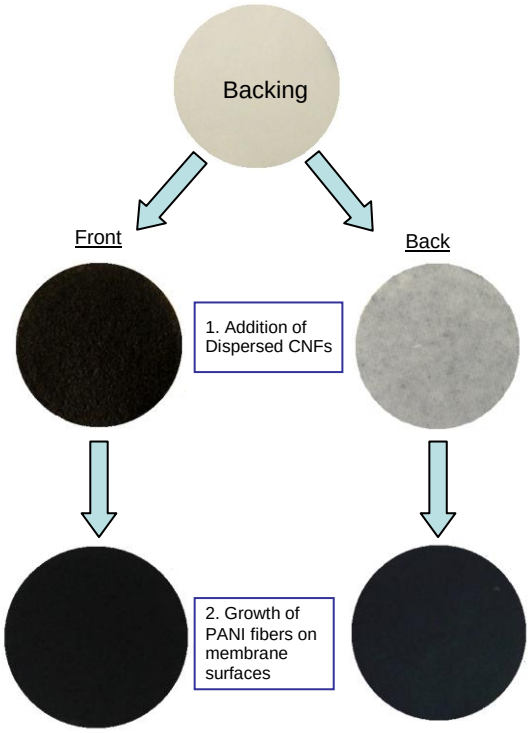

Figure 12: Formation of Composite Membranes

Thermally Cured Thin Film Membranes

First, purified nanofibers are prepared in the same manner as stated in the Polyaniline Nanofiber Synthesis section with the desired dopants. After purification, the nanofibers are centrifuged to remove the supernatant. The solution is then diluted 1:1 with deionized water. 5mL of the solution are pipeted in two portions, each of 2.5mL to the substrate, a 2 inch diameter silicon wafer. The water in the solution is then allowed to vaporize by letting the coated substrate sit for 24 hours. The substrate is then thermally cured using a hot plate at 260°C for one minute. The second 2.5mL coating is applied in the same manner described above. After the wafer reaches room temperature, the wafer is placed in water so the thin film can be removed from the substrate surface using a razor and a micro-spatula.

Contact Angle Measurement

The contact angle was measured using a sessile drop technique combined with a high-speed camera. The camera used was a COHU 4915-2000 and images were taken every 0.1 seconds. The images were then analyzed to find the most consistent contact angle as the water rapidly passed through the porous media. The contact angle and time when the contact angle was most constant was then used to compare various membranes.

Pure Water Flux

A dead-end filtration set-up was selected to facilitate the measurement of fouling. Pressure driven flow was achieved using a standard compressed nitrogen cylinder and a pressure gauge which read from 0-100 psi. The gas pressure was tightly controlled to generate a constant head of pressure in a sealed 4 or 10 liter Nalgene vessel. The cap of the vessel was equipped with a short gas inlet and a longer water outlet line. The tubing for the water outlet line extended to the bottom of the tank. The water outlet line feed to the top of a 10 mL Amicon dead-end 25mm membrane set-up. Prior to start-up, a membrane was placed in the Amicon unit, secured with an o-ring and sealed. The device is equipped with a relief value which is kept open during the course of the experiment. The start of the experiment begins when the compressed nitrogen valve was opened. In order to fill the 10 milliliter Amicon unit, the pressure relief valve was momentarily closed and immediately reopened. The initial time was recorded on a stop watch when the first drop of water exited the membrane unit. The setup is seen in Figure 13 and 14.

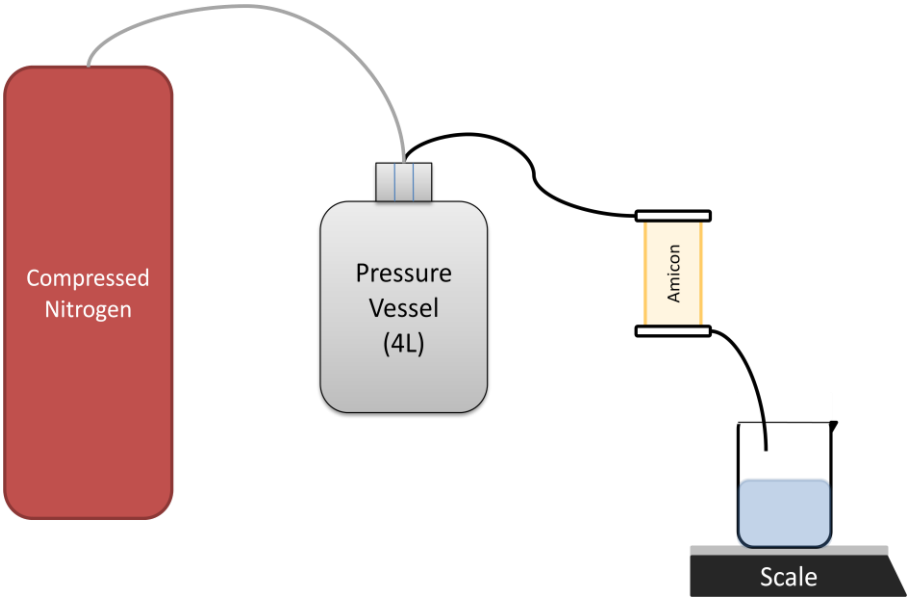

Figure 13: Experiment Set-up Schematic

Figure 14: Set-up Image

It should be noted that the vessel shown in Figure 14 is the 10L vessel used in the fouling trials. The change in mass was then measured over time at a given pressure using an electronic balance. When small flow rates were observed, a graduated cylinder was used to measure the volumetric flow rate. The pure water flux was determined by using MilliQ deionized water (18.2MΩ). The flux data was collected for at least ten minutes or two liters of water (whichever came first).

Fouling Trials

Fouling trials were run in the same manner described in the Pure Water Flux section, but with foulant water and a 10L vessel instead of a 4L vessel. The fouling of the membranes was determined by recording both the flow rate and the time of the reading to provide a measurement of the decrease in flux over time. The foulant water was prepared in two ways. First, in order to model natural water, locally available surface water was used. Olentangy river water collected around Woodruff Avenue was pre-filtered to remove all suspended particles and microorganisms larger than 0.45 microns. The filtration was accomplished using Pall Corporation High Capacity In-line 5µm and then 0.45µm filters. The pre-filtration set-up can be seen in Figure 15.

Figure 15: Pre-filtration of Olentangy River Water

The second foulant water was formed by dissolving 5mg of Suwannee River Humic Acid (SRHA) in 1 L of deionized water and mixed for 24 hours using a magnetic stir. For the trials with a pH of eight, the 3mmol of sodium bicarbonate was first dissolved in the deionized water prior to the addition of SRHA. The SRHA is a common model foulant used and cited frequently in membrane fouling publications. It is one of the reference humic acids available from the International Humic Substances Society.

Results

Thermally Cured Thin Film Membrane Synthesis

Several different synthesis conditions were examined to improve performance. The primary parameter investigated was the acid used in the synthesis. CH_3SO_3H was used for the majority of membrane synthesis trials. The ideal application volume of concentrated polyanline fibers was determined to be 5 mL on the 2 inch diameter silicon substrate by trial and error and observation. Several problems were encountered with uneven coating, resulting in the formation of pinholes. This was overcome by performing the coating in two applications, each with 2.5 mL and allowed to dry for 24 hours. While this membrane was uniform and free of pinholes, it still suffered from poor mechanical strength. Several attempts to measure the pure water flux were conducted, each resulting in mechanical failure at pressures between 10 and 20 atm. These pressures were necessary to generate flux across the membrane, yet only minimal flux was achieved, less than $5mL/(min*cm^2)$ at these higher pressures before mechanical failure occurred. An additional attempt was made to synthesize the membranes with HCl, but no significant improvement in mechanical properties was seen. An image of this type of membrane can be seen below in Figure 16. The second and third image in the series shows the mechanical failure which was common during the membrane synthesis process.

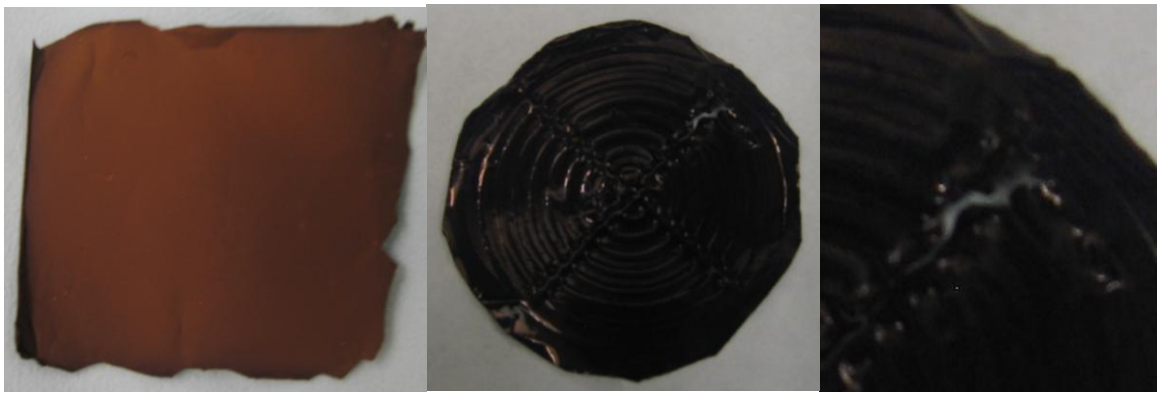

Figure 16: Image of Polyanline Thin Film Membranes with Tear

Additional investigation was performed to determine the affect of different forms of thermal curing, most notably the use of a convection to crosslink (using an oven), instead of the hot plate normally used. The use of an oven resulted in brittle membranes which were unusable; this idea was thus not pursued further. Thus, while many parameters were investigated to improve mechanical performance of these membranes, no dramatic improvement was achieved. Thus at the end of many synthesis experiments it was determined that the free-standing film simply presented too many challenges for the scope of this research.

Polyaniline Nanofiber Composite Membrane Synthesis

The polyaniline nanofiber composite membranes are composed of a support layer, a layer of carbon nanofibers (CNFs) and a final coating of polyaniline nanofibers. The parameters evaluated thus far include (1) the support material, (2) CNF binders/adhesives, (3) Dispersion of the CNFs, (4) coating thickness of CNF layer and finally (5) the synthesis conditions of the polyaniline (PANI) coating. While a fair amount of work has been conducted evaluating the first three parameters, additional work is necessary to understand the last two parameters.

Support Material

Several substrates have been evaluated for the support, or backing of the membrane. The support material is necessary because the active layer of CNFs and PANI nanofibers would not have enough material integrity to remain intact during the filtration process. The two most promising substrates for this role are Whatman #4 filter paper and a Novatexx polyester (PET) nonwoven. The PET substrate is the leading substrate in terms of robustness and the Whatman #4 filter paper allows the most even coating, hypothesized to be due to capillary action. The Whatman #4 was selected among all the cellulose-based filter papers because the pore size (20-25 μm) seems to offer the ideal substrate pore size distribution.

Adhesives

Several UV-curable optical adhesives were evaluated to act as binders for the carbon nanofibers. The original membranes suffered from detachment of the CNFs when the membranes were contacted with water or shear stress (example: handling with a micro-spatula). The two adhesives evaluated were Norland Optical Adhesive (NOA 72) and Ethylene glycol dimethacrylate (EGDMA) with a crosslinker. Both of these adhesives were cured with UV light. Dilutions in acetone and water with 5% -50% of adhesive were tested to decrease the viscosity of the solution,

and facilitate even coating. The adhesive was Norland Optical Adhesive diluted to10% by mass in acetone. The adhesives were diluted to reduce the viscosity and facilitate application.

Dispersion of Carbon Nanofibers

One of the most challenging aspects of synthesizing the membrane is creating an even coating of the CNFs. If the CNFs are not distributed evenly on the surface of the substrate, it is impossible to obtain an even pore size distribution. Thus, the flux is determined by the largest gaps in the CNF coating rather than the characteristic diameter of the pores created. The membrane on the right below in Figure 17 demonstrates an example of an uneven coating. The lighter batches on the surface (one is highlighted by the red box) represent regions of the membrane where the coating is not uniform.

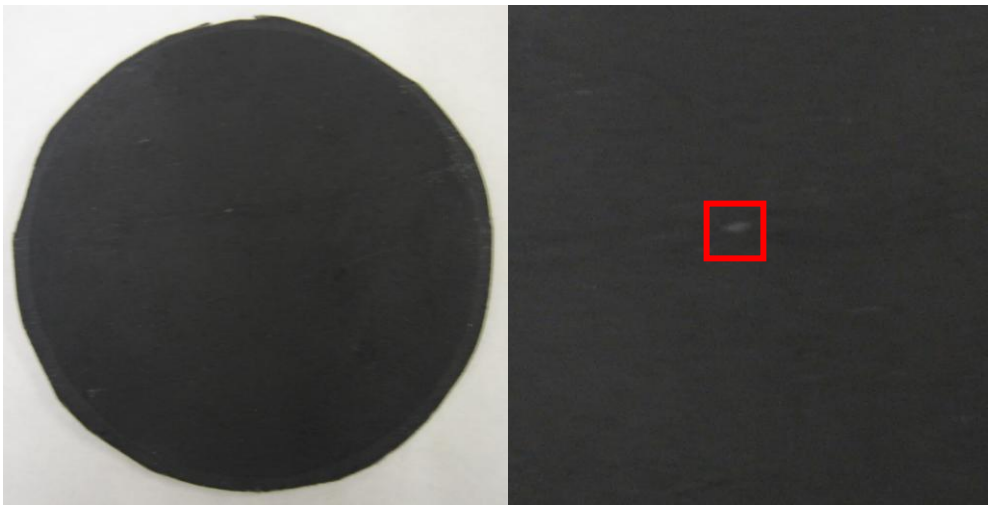

Figure 17: Substrate Coated Unevenly with CNFs

The most important indication of the quality of the CNF coating is the quality of the CNF dispersion in the carrier fluid. Due to the hydrophobic nature of CNFs, it is very difficult to obtain a stable dispersion in either acetone or water, due to the polarity of these solvents. While

it was possible to obtain a dispersion in acetone (less polar than water due to the carbonyl functional group) the CNFs quickly coagulated and precipitated to the bottom of the vial. To create more stable dispersions, several dispersants were evaluated, including Poly(sodium 4-styrene sulfate), Triton X-100 and Sodium Dodecyl Sulfate (SDS). Additionally, with the horn sonicator in the NSEC facility, a stronger sonication method was evaluated. The results from the dispersion trials are summarized below in Table 1.

CNF Mixture				Result
Solvent	**Dispersant**	**wt% CNF**	**Sonication Method**	
Water	None	0.1-2.0%	Bath (full amplitude)	Very Poor
Acetone	None	0.1-5.0%	Bath (full amplitude)	Decent at lower wt%, but unstable
Water	Poly(sodium 4-styrene sulfate)	0.1-2.0%	Bath (full amplitude)	Slightly improved, but unstable
Acetone	Triton X-100	0.1-2.0%	Bath (full amplitude)	Slightly improved, but unstable
Acetone	None	0.10%	Horn (85% amplitude)	Unsuccessful, CNFs still clumped and precipitated
Water	Sodium Dodecyl Sulfate (SDS)	0.50%	Horn (85% amplitude)	Successful, mixture stable & CNFs remain dispersed

Table 1: Summary of Sonication Experiments

The most successful recipe was 0.50 wt% CNF with 0.50 wt% SDS in diH_2O at 85% amplitude using the horn sonicator. This recipe was used to synthesize the remainder of the membranes discussed below. An adhesive is not currently used for the first set of results because improving the dispersion, also greatly improved the adhesion of the CNFs without the addition of a binder.

As previously stated, the substrate chosen for further evaluation was Whatman #4.The chosen mixture was composed of 0.50 wt% CNF with 0.50 wt% SDS in diH_2O. It is difficult to control the amount of CNFs deposited, but it was determined that ten grams of the solution described above consistently gives an even coating.

Composite Membrane Results

Pure water flux results from different trials can be seen in Table 2.

Membrane	Pressure (psi)	Flow (g/min)	Std. Dev
Whatman #4	10	513.36	5.93
CNF #1	10	6.36	0.21
CNF #2	10	6.19	0.60
CNF & PANI #1	10	6.71	0.38
CNF & PANI #1	10	6.83	0.28
CNF & PANI #1	15	9.00	0.45
CNF & PANI #1	20	9.71	0.45
CNF & PANI #2	10	4.70	0.28
CNF & PANI #2	20	11.80	0.28
CNF & PANI #2	30	14.43	0.25

Table 2: Summary of pure water flux data

Not shown on the above table, one batch of membranes exhibited mechanical failure while testing due to the pressure differential. This failure indicates that the CNF thickness may play a key role in mechanical integrity of the membranes. The fouling was also measured for these membranes. This data is presented below in Figure 18.

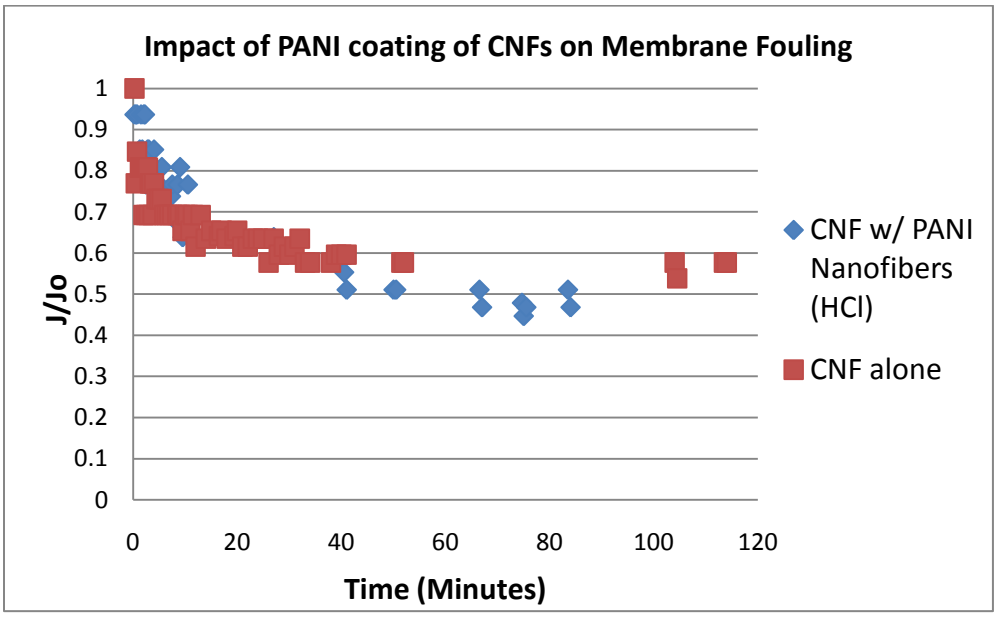

Figure 18: Coated vs. Uncoated Composite Membrane Fouling

Due to the difficulties in obtaining consistent CNF deposition between batches, further trials to determine the impact of different parameters affecting the polyaniline nanofiber coating were determined using commercially available membranes.

PANI Nanofiber-Coated Commercial Membranes

SEM Results

SEM images of the three membranes can be seen below in Figures 19-21. The coating of the Anodisc ceramic membrane resulted in a significant reduction of flux, indicating a significant blockage of pores (seen also in the SEM). Thus, it was decided not to investigate the performance of the ceramic membranes in greater detail. In general, the SEM images confirm that the polyaniline nanofiber coating is about 10 nanometers.

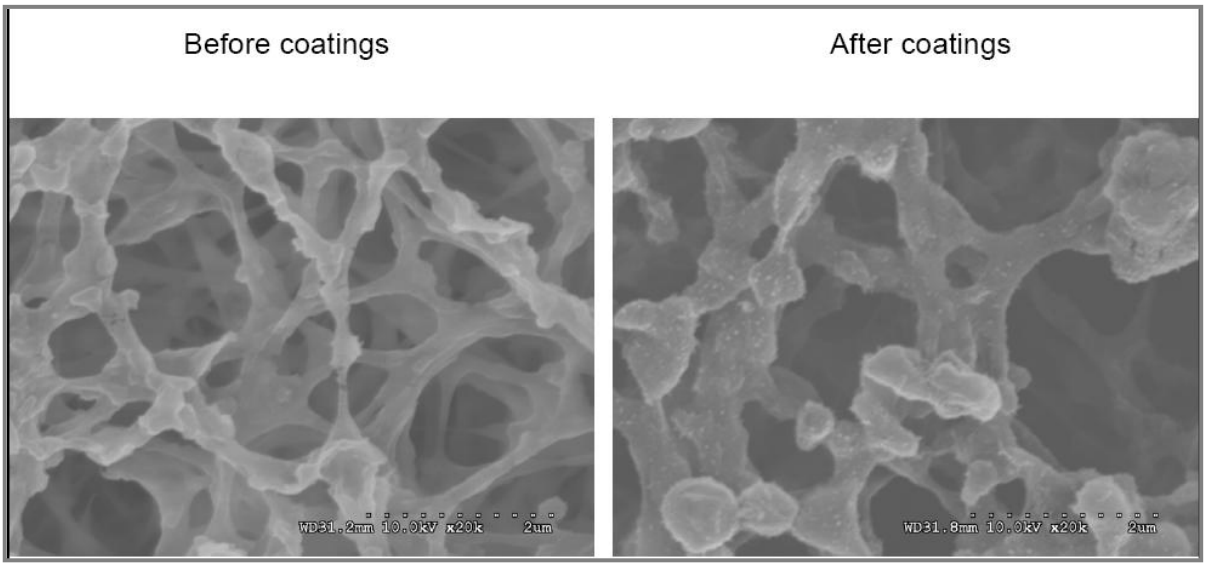

Figure 19: SEM Image of 0.45µm Cellulose Ester Membrane

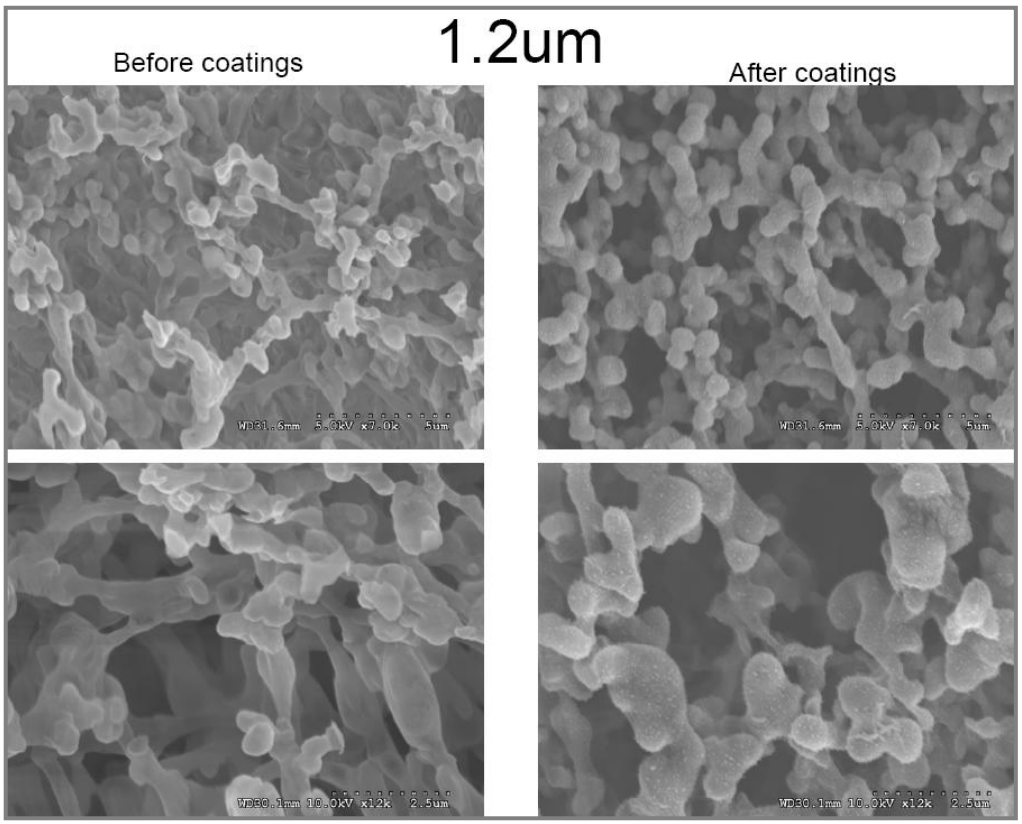

Figure 20: SEM Image of 1.2µm Cellulose Ester membrane

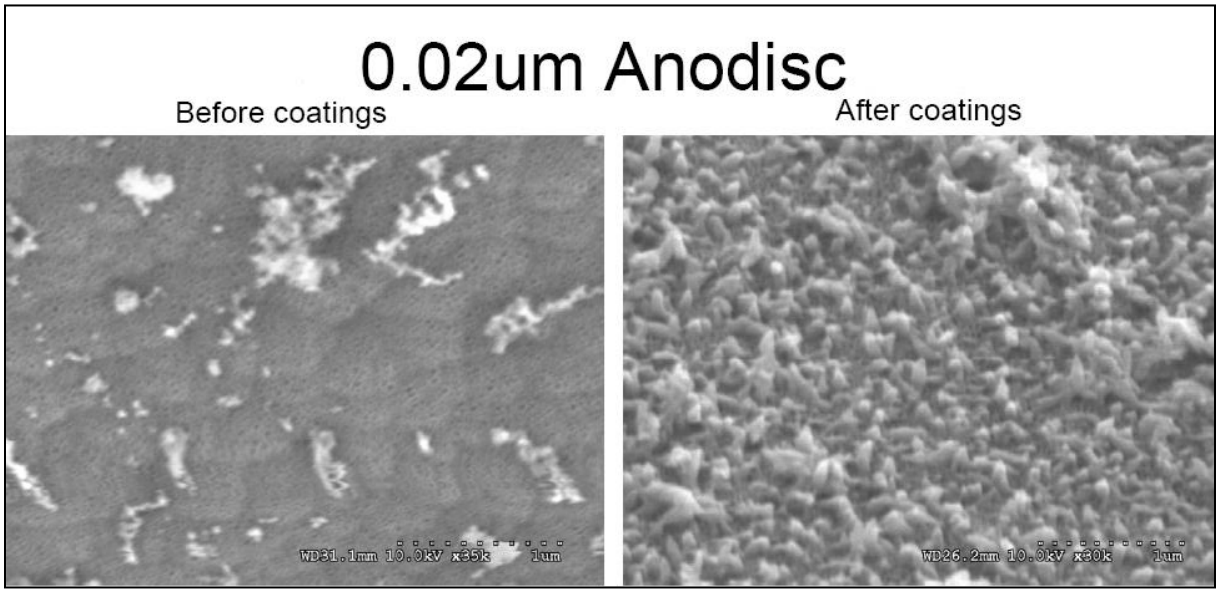

Figure 21: SEM Image of 0.02µm Anodisc Ceramic Membrane

Contact Angle Results

The contact angle of commerical and coated membranes were evaluated to see if the coated commerical membranes exhibit a greater hydrophilicity than the uncoated membranes. The results of these tests are presented below captured by a highspeed camera. These results are sumarized below in Figure 22.

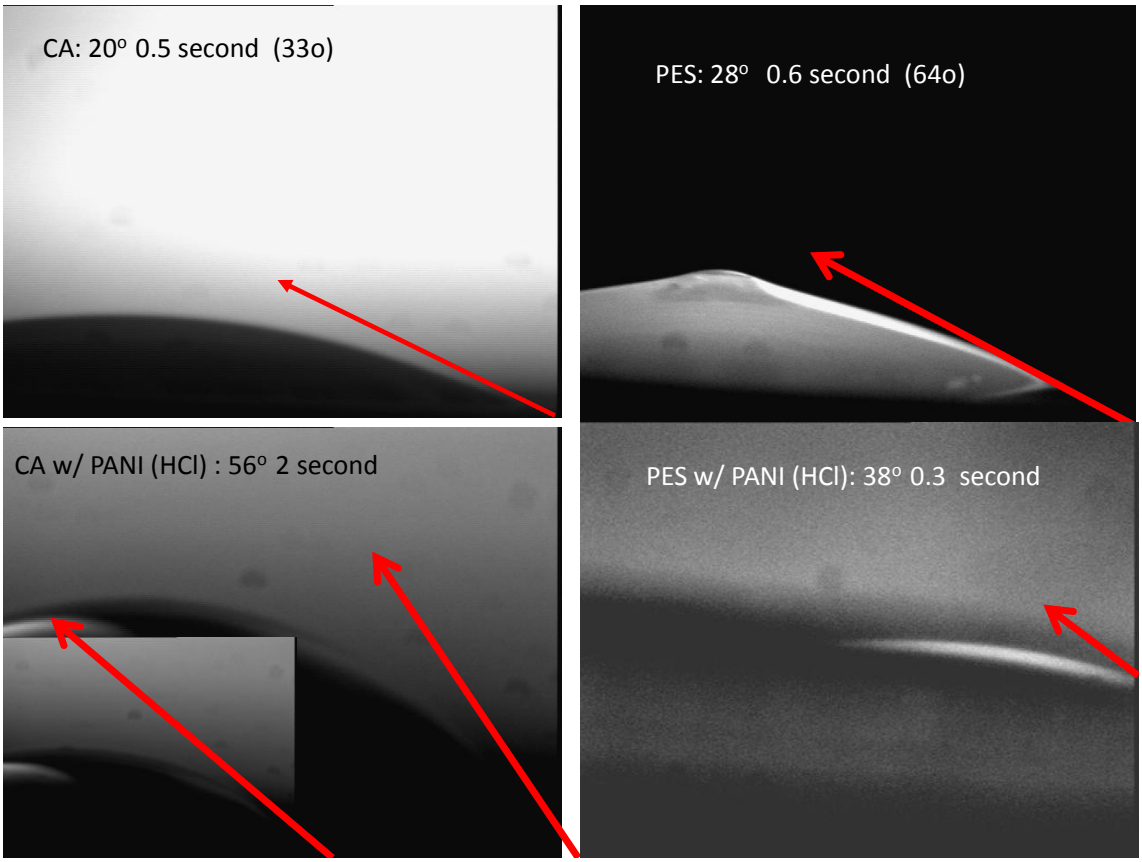

Figure 22: Contact Angle Results

The contact angle of the PES membrane without a coating was found to be 28°. This is slightly lower than the published contact angles of 44.7°-69.7°. The PES contact angle increased with the PANI coating to 38° signfying that the coated membrane is slightly more hydrophobic. The uncoated CA membrane was the most hydrophilic membrane. The contact angle was found to be

20° which is again much less than the values of 46°-53.3° in literature. The contact angle increased to 56° with the PANI nanofiber coating. The uncoated contant angle values suggest that a more precise contact angle measurement method should be developed, or that the membranes need to be more thoroughly cleaned or dried prior to testing. Another method recommended for evaluating the hydrophilicity of the coated and uncoated membranes is the static contact angle techique. The increase in contact angle with the PANI coating suggests that the PANI nanofibers increase the hydrophobity of the CA and PES membranes.

Fouling Trials with Filtered Olentangy River Water

The results from the pure water flux of all the membranes are presented below in Table 3. These values are important for determining the initial flux value, J_o, for analyzing the fouling data.

Name of Membrane	**Pure Water Flux (mL/(cm^2*min)**
$HClO_4$ coated membrane	33.3
PAAS coated membrane	51.9
DBSA coated membrane	47.4
MSA coated membrane	53.7
NSA Double coated membrane	16.0
HF coated membrane	49.2
PAS Double coated membrane	17.7
HCSA Triple coated membrane	48.6
Reference: 0.45um membrane	53.2

Table 3: Pure Water Flux of Coated 0.45µm membranes with alternative acids

The fouling data can be seen in Figure 21 and Figure 22. Membranes tested here are Millipore mixed cellulose esters, 0.45µm and 1.2µm pore sizes, in Figure 21 and Figure 22, respectively. The coating is PANI nanofibers with perchloric acid ($HCl0_4$) as the dopants. The fouling trials were completed with filtered Olentangy River water.

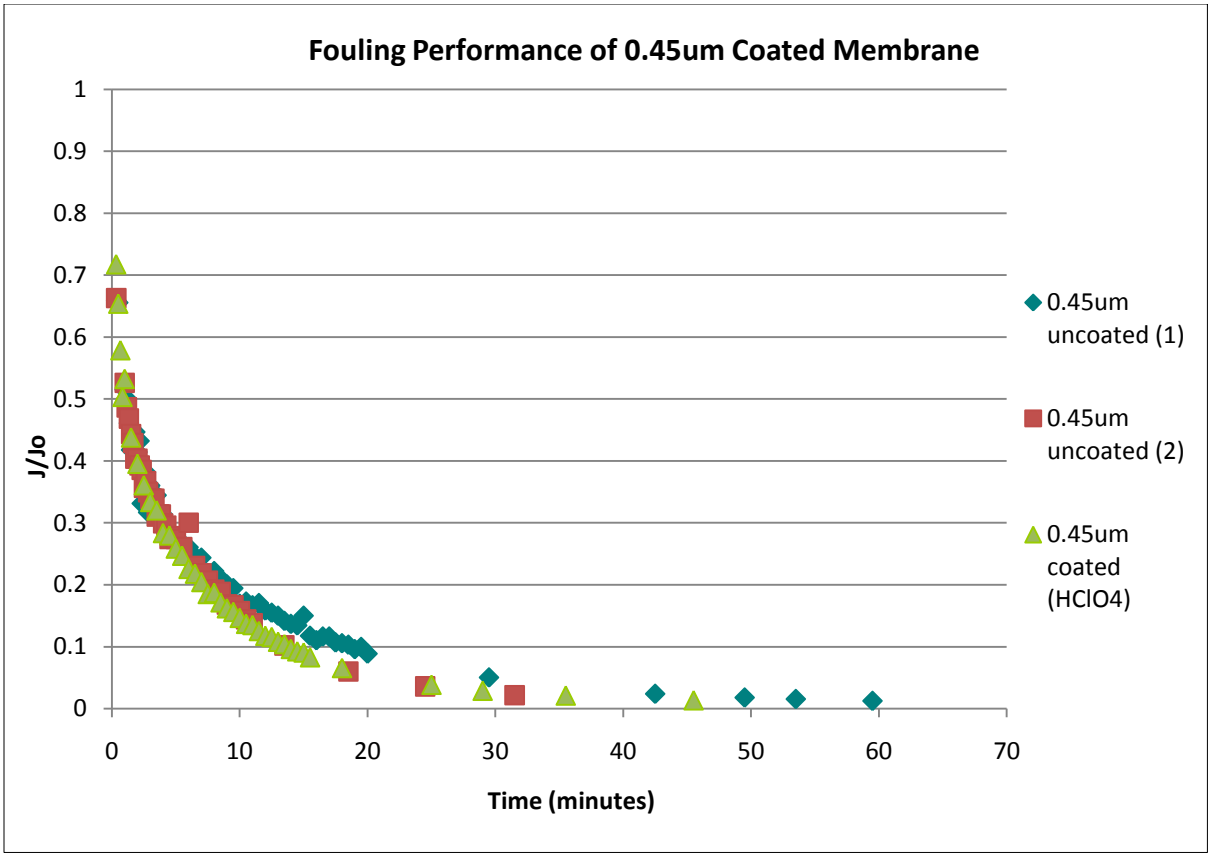

Figure 23: Fouling Performance of 0.45µm membrane

In Figure 23, it the two uncoated 0.45µm cellulose ester membranes show relatively consistent trends with respect to fouling. The PANI nanofiber coated membrane shows comparable fouling with Olentangy River water to these two membranes within the error of the measurement, but unfortunately, no improvement was observed.

The impacts of PANI coatings on larger membranes was also investigated. The fouling performance of a 1.2µm cellulose ester membrane is seen in Figure 24.

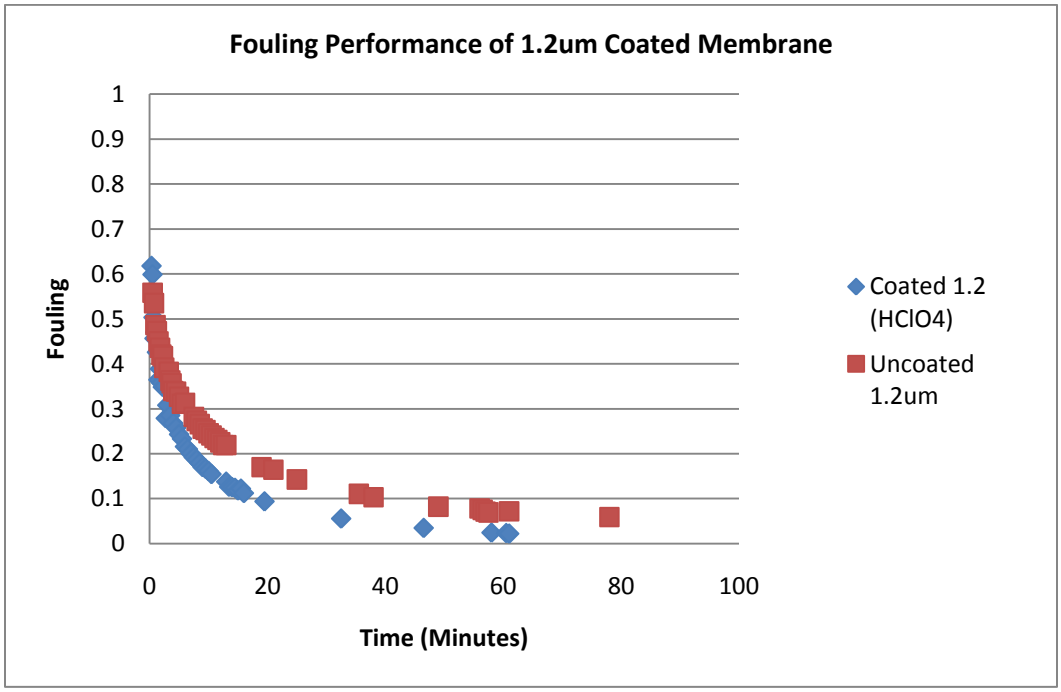

Figure 24: Fouling Performance of 1.2µm membrane

When the PANI coating was invested for larger pore membranes, specifically 1.2µm cellulose ester membranes, a decrease in performance was observed when using Olentangy river water.

Different dopant acids were investigated to improve fouling performance of the membrane. These dopants control the speed and mass of the PANI nanofiber growth. Using Olentangy River water, membranes synthesized with a myriad of acids were tested against the uncoated reference Millipore 0.45µm membrane. These results can be seen in Figure 25.

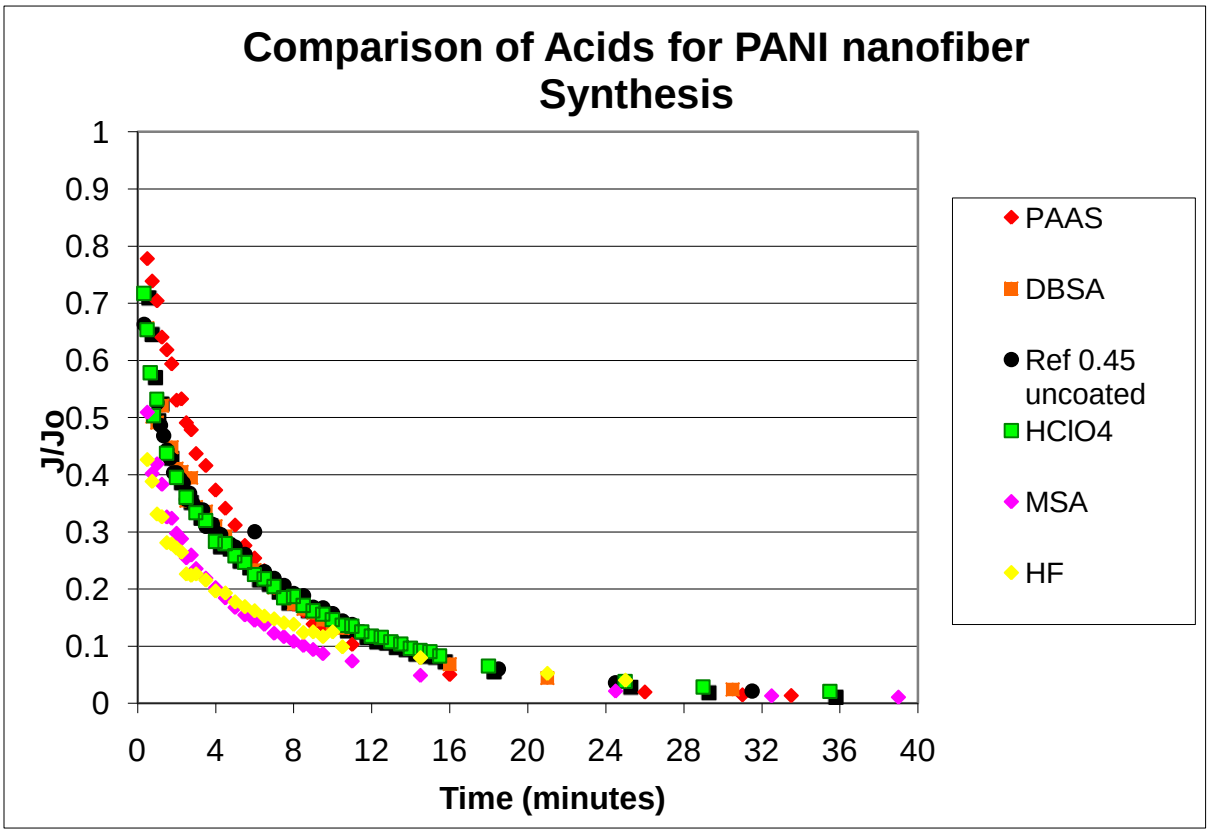

Figure 25: Fouling Performance of 0.45µm membrane with different acids

The majority of dopants investigated made little or no impact on membrane fouling with Olentangy River water. The best PANI coatings for fouling were formed with the larger organic acids which slowed the growth of PANI nanofibers and resulted in thinner coatings. In this investigation, less PANI or no PANI fouled the least.

Another idea investigated was using double or triple polyaniline nanofiber coatings. The results from the double layer technique can be seen in Figure 26. The double coating reduced the fouling but also reduced the pure water flux from 53.2 to 17.7 mL/(min*cm^2).

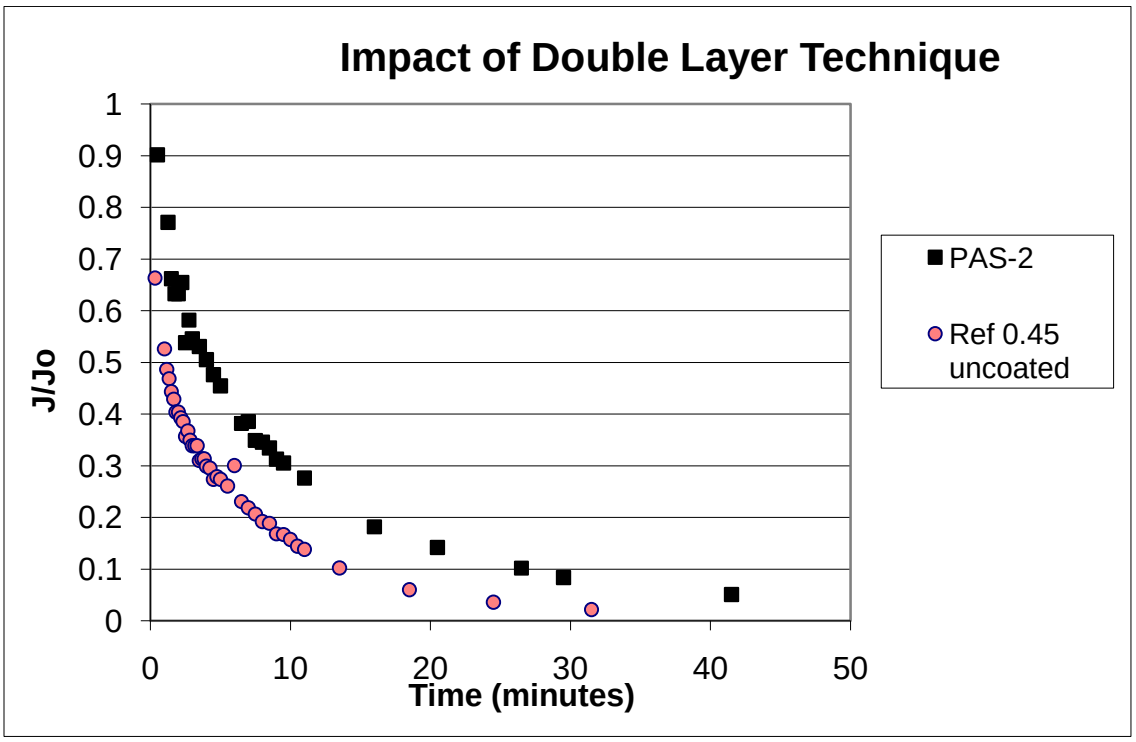

Figure 26: Fouling Performance of double coated 0.45µm membrane

While the fouling appears to decreases less with respect to time it is hard to compare the two different pore sizes because less water, and thus less foulant, actually passes through the membrane.

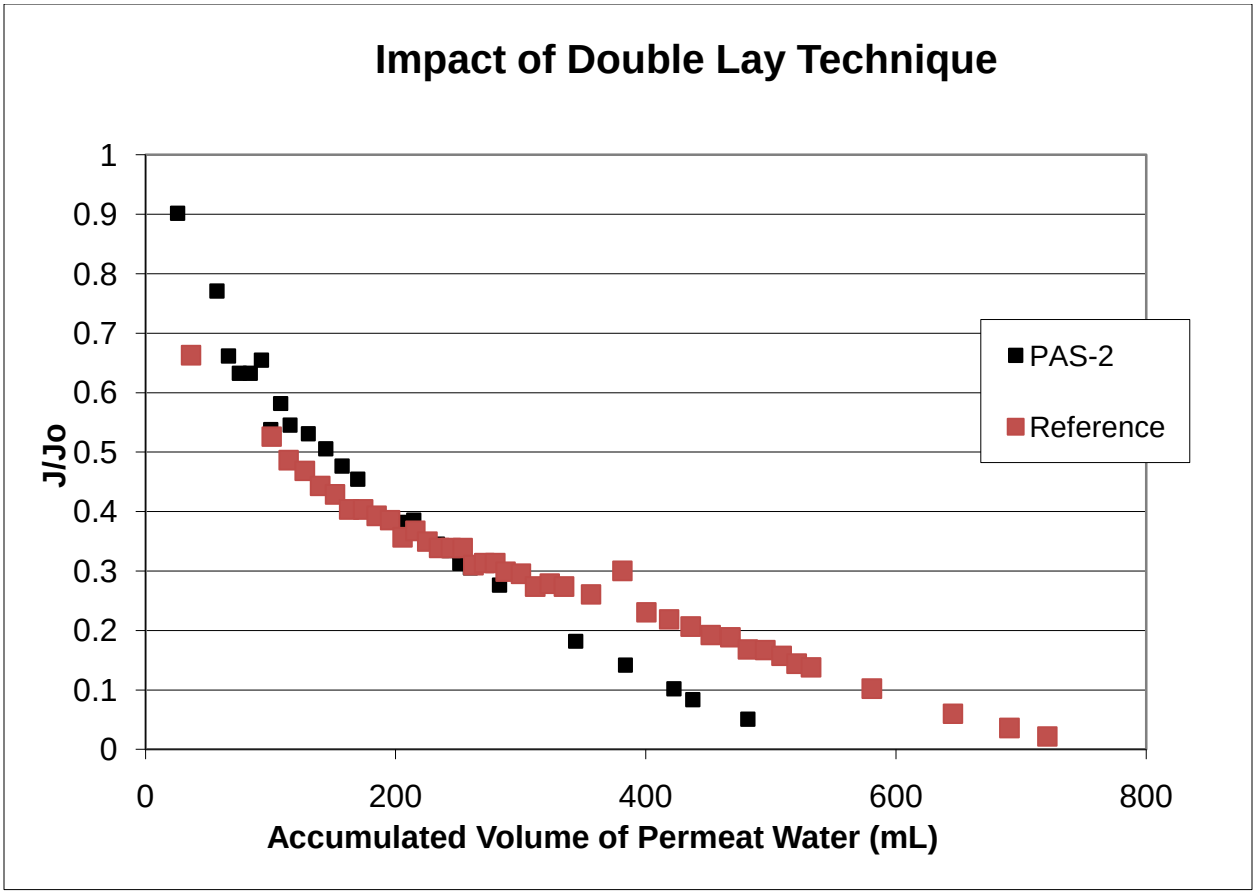

Figure 27: Fouling and Volume Performance of double coated 0.45µm membrane

In Figure 27, the ratio of initial to final flux is compared with the total volume of permeate. When investigating the performance of the membrane with respect to the permeate volume passed through the membrane instead of the time passed, the performance

Fouling Trials with Humic Acid

In addition to trials with Olentangy River water, fouling trials were carried out using Suwannee River Humic Acid (SRHA) reference. Three dopants were evaluated in this experimentation, hydrochloric acid (HCl), PSA Poly(4-styrenesulfonic acid) solution (PSA), and 4-Dodecylbenzenesulfonic acid (DBSA) to compare the impact of different PANI nanofiber coatings on membrane performance. The membrane evaluated for these coatings was a 0.45µm Polyethersulfone (PES) membrane. In addition to testing the impact of three dopants, the impact of the doped state, as well as the pH of the foulant solution was investigated. First, the pure water flux for the seven membrane types were determined and are listed below in Table 4.

	Flow (mL/min)		
	Dedoped	**Doped**	**% Change**
PES 0.45µm with PANI (HCl)	26.02 ± 0.90	36.95 ± 2.25	**-29.6%**
PES 0.45µm with PANI (PSA)	11.55 ± 0.18	10.43 ± 0.06	**8.7%**
PES 0.45µm with PANI (DBSA)	101.46 ± 3.11	26.02 ± 0.90	**139.0%**
PES 0.45µm Reference	97.13 ± 2.57		

Table 4: Impact of Doped State on Pure Water Flux of Membranes

The removal of the dopant increased the flow through the membrane for PANI coatings with PSA and DBSA by 8.7% and 139.0% respectively. This is hypothesized to be due to the removal of the large organic functional groups which are generally more hydrophobic and may impede the flow of water. The flow increased in the doped state using HCl as the dopant. The removal of the smaller chlorine counter ion does increase the flux as seen for the larger counterions. Instead, the dedoped stated has a slower flow suggesting the doped PANI structure is preferred as long as the counterions are not large and nonpolar.

The impact of the PANI coating on fouling, including the effect of the dopant and doped state, was also investigated for the PES 0.45µm membranes. The fouling of the membrane was first carried out using un-buffered deionized water with a pH of around 6 and a solution of 5 mg/L of SRHA. The fouling results of the PANI coated membranes with DBSA and HCl against the reference membrane can be seen in Figure 28.

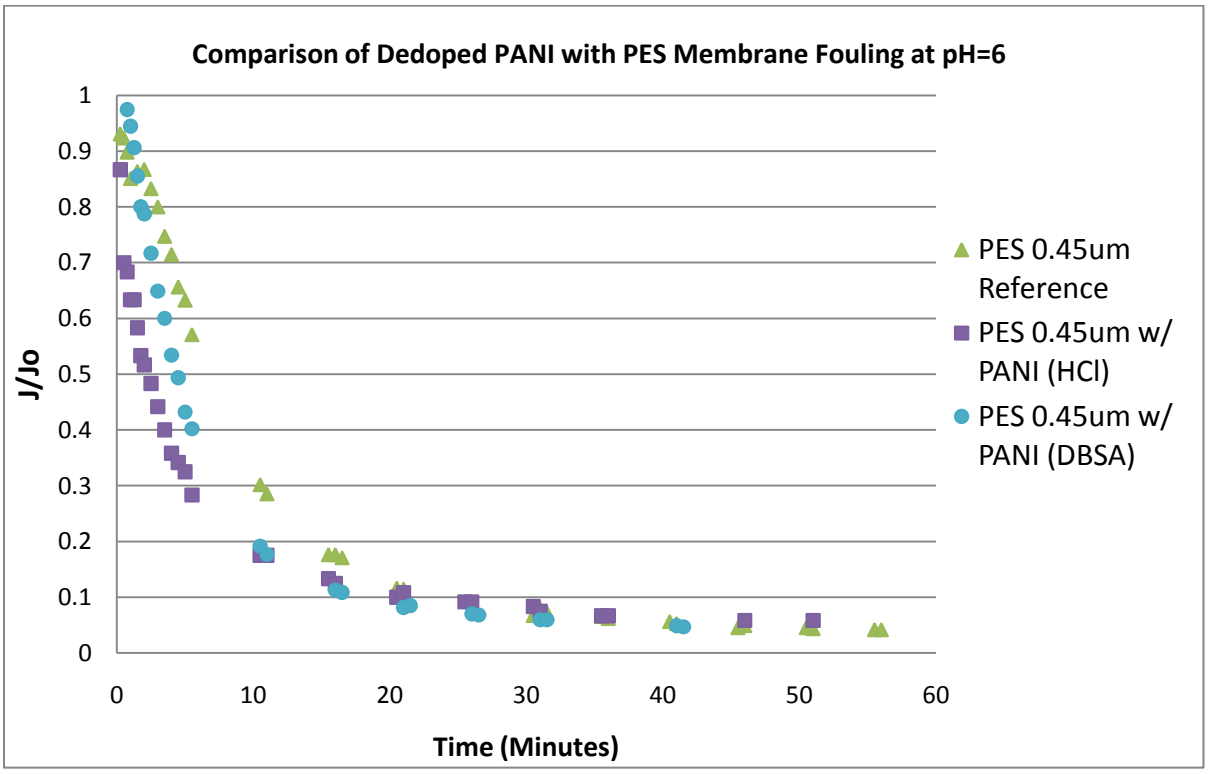

Figure 28: Impact of Doped State on Fouling

The PES reference performed better than both of the PANI coated membranes. The PANI nanofiber coatings synthesized with DBSA performed better than the membrane synthesized with HCl. This is most likely due to the fact that the PANI coating is much thinner for the DBSA synthesized membranes. This coating is thinner due to the slower growth of the nanofibers in the DBSA acid than the HCl.

The impact on of the doped state on fouling was investigated for the PANI synthesized with HCl. These results are can be seen. In can be seen in Figure 29

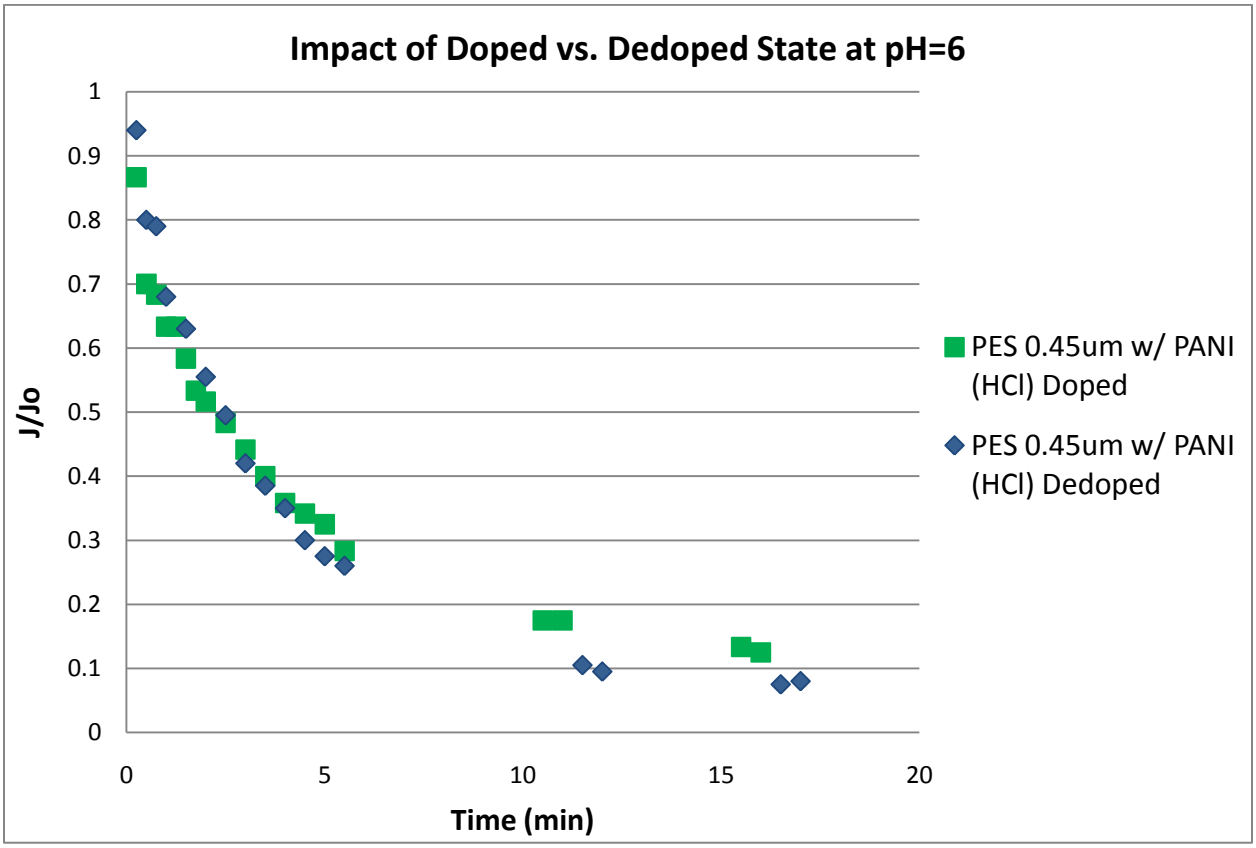

Figure 29: Impact of Doped State on Fouling

There was no obvious difference in the fouling between the two doped states when looking at fouling with respect to time using SRHA.

The impact of the pH was determined by the addition of sodium bicarbonate to raise the pH of the foulant solution to approximately 8. The impact of the two pH values on the reference PES 0.45µm membranes is seen below in Figure 30.

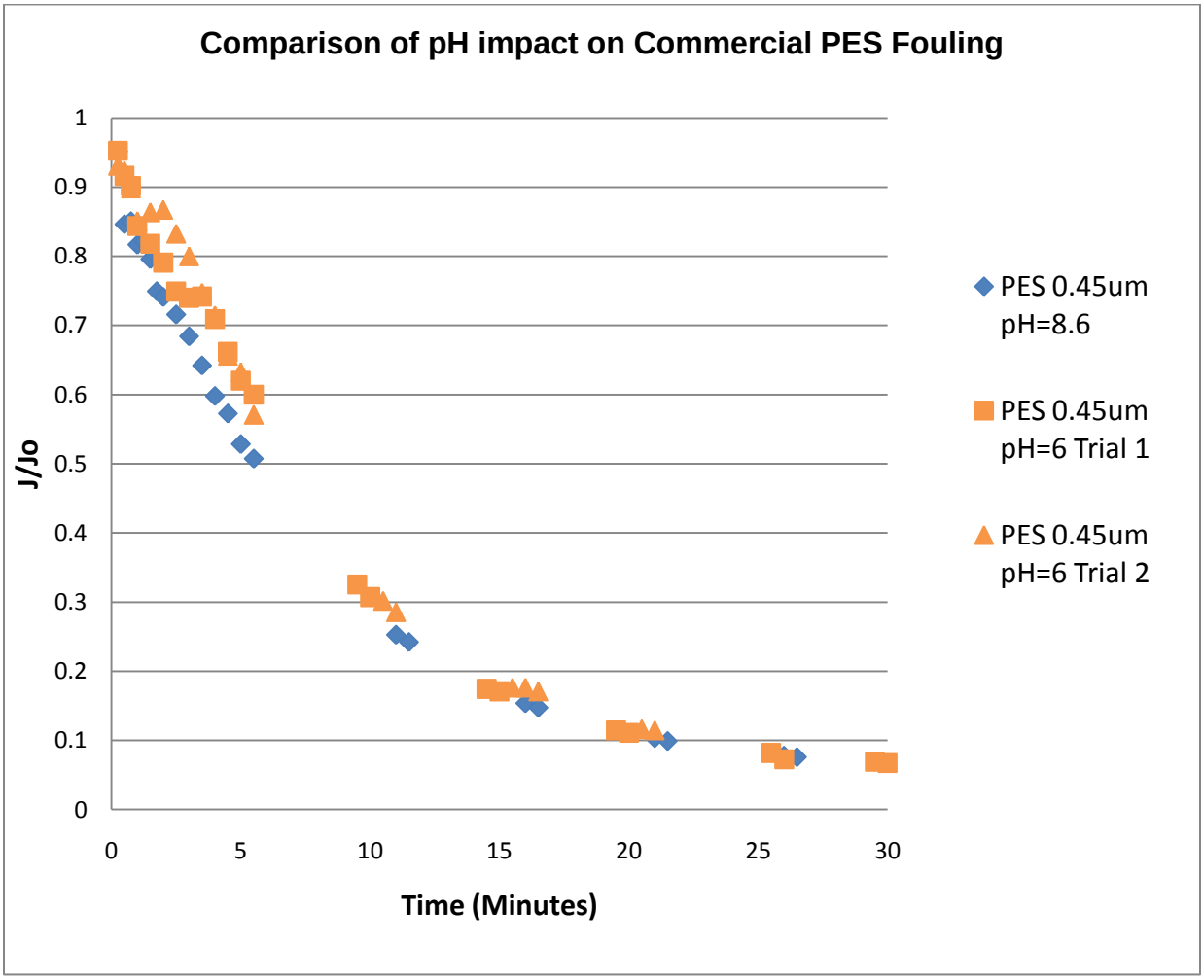

Figure 30: Impact of pH on Fouling of PES Membranes

While increasing the pH was expected to decrease the fouling, no significant trend was observed. This is perhaps due to the fact that a lower concentration of SRHA, only 5 milligrams per liter, was used.

The impact of the change in pH on the PES 0.45µm membranes coated with PANI (HCl dopant) was also investigated. A comparison of fouling at pH values of 6 and 8.6 can be seen in Figure 31.

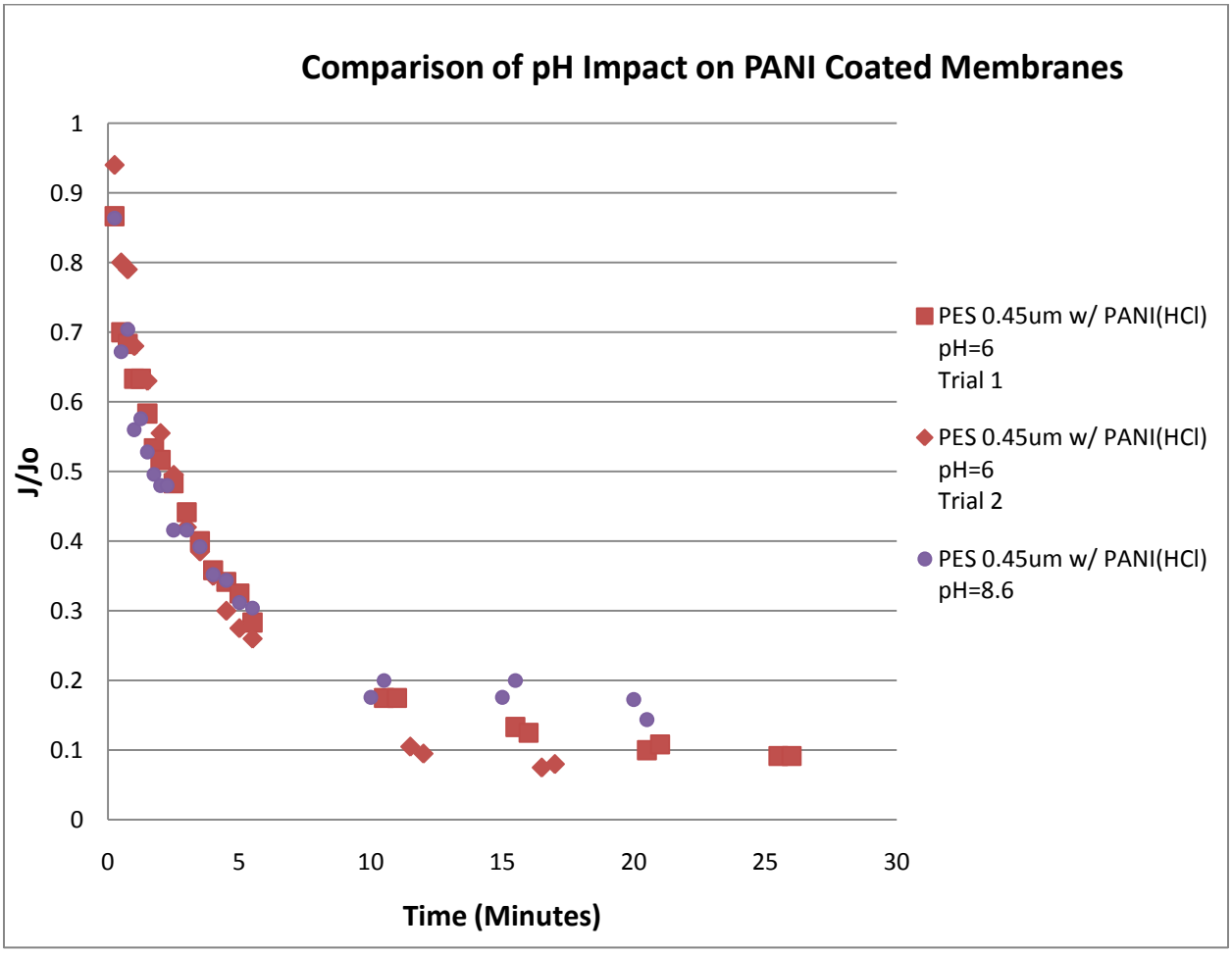

Figure 31: Impact of pH on Fouling of PANI Coated Membranes

Increasing the pH of the PANI coated membranes made no difference in the fouling during the first five minutes and only slightly improved fouling after five minutes. Again, a greater impact of pH on the fouling of the PANI coated PES membranes may be observed with a higher concentration of SRHA.

Discussion and Conclusions

For the thermally-cured thin film membranes, the best acid for use during synthesis was CH_3SO_3H applied on a silicon substrate in two portions. This approach provided an even coating with no pinholes, yet the mechanical performance of these membranes was still quite poor, resulting in the tearing of the thin film when under pressure for filtration operation. It does not appear that the mechanical performance can be improved by thermal curing using the current approach because the pores simply become too small and obstruct the water flow. Thus, more innovative work is needed to improve the mechanical properties of the thin film membranes before further conclusions can be made.

The experimentation with the dispersion of carbon nanofibers identified the 0.5wt% CNF with 0.5wt% SDS in deionized water proved to be the best mixture. When sonicated with a horn sonicator at 85% amplitude this method provided the highest quality dispersion. This is due to the ability of the surfactant, SDS, to decrease the hydrophobic interaction of the CNFs with the solvent, and the increased dispersive energy of the horn sonicator. After the CNFs were properly dispersed on the substrate, preliminary testing of the performance with and without the PANI coating was performed. As seen in Figure 15 the PANI coating with hydrochloric acid actually increased the fouling observed. This phenomenon is not understood, but some possible explanations exist. First, that the relatively high hydrophobicity of the uncoated CNF membrane may be able to reduce fouling with humic acid due to the amphiphilic nature of the molecule. Second, that some residual surfactant may have been present on the CNF surface that would assist in deterring fouling. While the membranes were both washed, it is much less likely that the surfactant remained on the coated membrane under the harsh acidic conditions necessary for the PANI nanofiber synthesis. The third possible explanation is that the PANI nanofibers interact

with the NOM species, specifically humic acid in this circumstance to increase fouling. This third explanation is confirmed by later trials with cellulose-based and PES membranes.

The results from the SEM images confirm that when using the perchloric acid, nanofiber growth is approximately 10 nm in each direction, seemly decreasing the nominal pore size by 0.02μm. This coating significantly reduces the flux of the 0.45μm cellulose ester membrane from 53.2 to 33.3 mL/(cm^2*min). The PANI nanofiber coating with perchloric acid also increases the fouling for the 0.45μm and 1.2μm cellulose ester and 0.45μm PES membranes. Additionally, the results from Figure 22 show that while some acids provide better performance than others (PAAS provided the best results) there was not a dramatic improvement over the uncoated reference. In order to better understand this behavior, the impact of the doped state and pH were investigated in greater detail.

Three dopants, hydrochloric acid, 4-Dodecylbenzensulfonic acid and Poly(4-styrensulfonic acid) were used to evaluate different PANI nanofiber coatings on PES membranes. It was found that the dedoped state allows a greater pure water flux except when large organic counterions are attached in the doped state. The structures of 4-Dodecylbenzensulfonic acid and Poly(4-styrensulfonic acid) can be referenced in Figure 32 below.

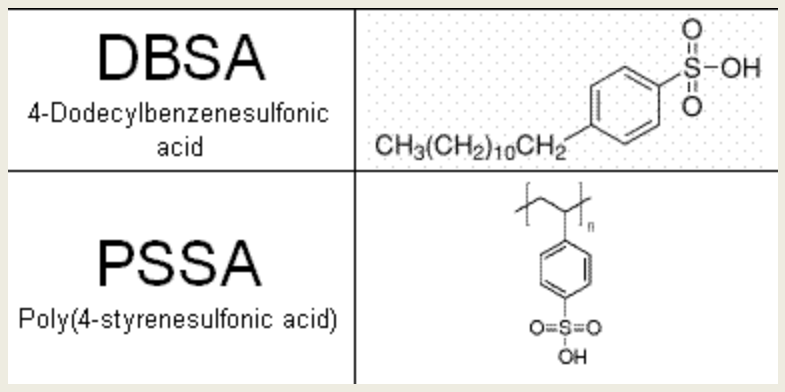

Figure 32: Structure of Dopants

For the two trials the DBSA and PSSA doped membrane, flux actually increased, suggesting the removal of the large hydrocarbon-based counterions. These groups are hydrophobic and expected to decrease the flux. This suggests that there is an effective removal of the counterions after ammonium hydroxide is used.

It was also determined that increasing the pH slightly decreased the fouling of the PES and PANI nanofiber-coated membrane, but no significant impact was observed. Although no dramatic change in fouling was observed at the current humic acid level for either the reference or coated membranes, it is possible that a greater impact may be observed by running the trials at 25mg/L SRHA as done in literature instead of 5mg/L SRHA .

While PANI nanofiber coatings synthesized with DBSA performed better than the nanofiber coatings synthesized with HCl, both fouled worse than the reference membrane. Since the DBSA dopants results in much slower growth of the nanofibers than HCl or $HClO_4$, the coating thickness is also much smaller. Thus, it is difficult to say if the DBSA dopants forms better quality nanofibers than HCl, or if the performance is simply a function of the total quantity of nanofibers. The data indicates that PANI nanofibers decrease performance in almost every

scenario, so it is logical that less of the PANI nanofibers would provide greater performance. The exceptions are the double and triple PANI nanofiber coated membranes where multiple coatings were performed in succession. These membranes performed better in the fouling trials, but also significantly reduced the pure water flux. Thus, the reduction in fouling may be attributed to the much smaller poor size, since membranes in the smaller pore size range generally suffer less fouling consequences due to NOM adsorption.

There are two proposed explanations for the increase in fouling for the PANI nanofiber coated membranes. First, the idea previously suggested that the PANI nanofibers interact with humic acid molecules to attract rather than repel them. The second explanation is that since the PANI nanofiber coatings do not actually increase the hydrophilicity of the cellulose-based and PES membranes, that the hydrophobicity of the coated membranes controls the fouling. The contact angle measurements showed that the PANI nanofibers coating increased the contact angle for both the 0.45um PES and Cellulose Acetate membranes. This suggests that the originally super-hydrophilicity reported for the composite membranes depends much on the surface roughness as shown in Figure 1. Since the super-hydrophilicity is not present in the coated membranes, it may not be possible to compare the impact of different PANI nanofiber parameters on this substrate. Within the scope of this investigation, PANI did not improve membrane fouling performance, but future study of its novel properties for water purification applications is recommended.

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